ISOMER-SPECIFIC IR SPECTROSCOPY OF BENZENE-(WATER)$_N$ CLUSTERS WITH *N*=1-8: NEW INSIGHTS FROM THE WATER BEND FUNDAMENTALS AND ISOTOPICALLY SUBSTITUTED CLUSTERS

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This talk will focus on the isomer-specific IR spectra of benzene-(water)n (BWn) clusters with n = 1-8, returning to a topic studied by our group[a] some 20 years ago, but now with higher resolution (OH stretch region), with inclusion of data from isotopically substituted clusters, and with extension into the HOH bending mode region. Spectra are recorded using resonant ion-dip infrared spectroscopy, an IR-UV double resonance method. Isomer-specific IR spectra in the regions of OH, OD stretches and HOH, HOD bend of benzene-H_2O, -D_2O, -HOD, -$(H_2O)_2$, -$(D_2O)_2$, -HOD-DOD were recorded in order to investigate in greater detail the intermolecular potential energy surface between water and benzene. These spectra show strong combination bands in addition to the OH/OD stretch fundamentals arising from large-amplitude "tumbling" and tunneling along internal rotation and torsion coordinates of water(s) on the surface of benzene. Interestingly, the number of extra bands and spectral patterns change dramatically depending on cluster size, the kind of deuterated isomer, and the spectral region probed. In larger clusters with n=3-8, the water HOH bending region is explored for the first time. The prominent bending mode transitions in BW1-8 are spread over a relatively small range (1610-1660 cm^{-1}), and shift with cluster size in a way that reflects the known structural changes that accompany the increase in size. By comparison of experiment with calculation, it is possible to assign the experimentally observed 1614 cm^{-1}transition of BW1 and 1615 $cm^{-1}$of BW2 bands to the π-bound water molecule. The 1620-1660 cm^{-1}bands of BW3-8 are due to water molecules that can be categorized as single-acceptor, single-donor (AD) hydrogen-bonded waters. In the case of single-acceptor, double-donor (ADD) water molecules, which are expected to be seen from BW6,[a] they show higher-frequency bending vibrations and weaker IR intensity, which would correspond to very weakly observed bands in 1660-1750 $cm^{-1}$for BW6-8.

[a]R. N. Pribble and T. S. Zwier, Science, 1994, 265, 75-79.